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August 02, 2004

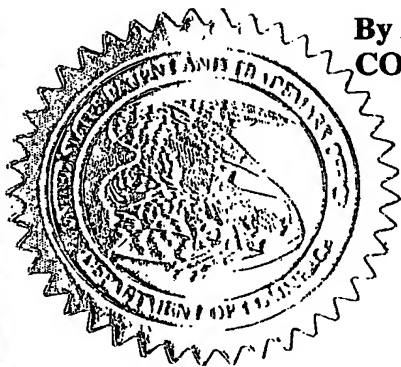
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APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE.**

APPLICATION NUMBER: 60/471,797

FILING DATE: May 19, 2003

RELATED PCT APPLICATION NUMBER: PCT/US04/16409

**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**



M. Tarver

**M. TARVER
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PTO/SB/16 (10-01)

Approved for use through 10/31/2002. OMB 0851-0032

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

Express Mail Label No. EU5999925515US

INVENTOR(S)				
Given Name (first and middle (if any))	Family Name or Surname	Residence (City and either State or Foreign Country)		
CHARLES D.	LANG	GOLETA, CALIFORNIA		
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto				
TITLE OF THE INVENTION (500 characters max)				
HOLE INJECTION LAYER WITH IMPROVED PERFORMANCE FOR POLYMER LIGHT EMITTING DIODE DISPLAYS				
Direct all correspondence to:		CORRESPONDENCE ADDRESS		
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ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification Number of Pages		<div style="border: 1px solid black; padding: 2px; display: inline-block;">7</div>		<input type="checkbox"/> CD(s), Number
<input type="checkbox"/> Drawing(s) Number of Sheets		<div style="border: 1px solid black; padding: 2px; display: inline-block;"></div>		<input checked="" type="checkbox"/> Other (specify)
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76		<div style="border: 1px solid black; padding: 2px; display: inline-block;">Return Receipt Postcard</div>		
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT				
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees				
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:		<div style="border: 1px solid black; padding: 2px; display: inline-block;">04-1928</div>		<div style="border: 1px solid black; padding: 2px; display: inline-block;">160.00</div>
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
<input checked="" type="checkbox"/> No.				
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____				

Respectfully submitted,

Date 05/19/03

SIGNATURE

THOMAS H. MAGEE Reg. No. 27,355 for MARY ANN CAPRIA

TYPED or PRINTED NAME MARY ANN CAPRIA

REGISTRATION NO.

32,659

(If appropriate)

Docket Number

UC0330 US PRV

TELEPHONE 302-992-3749

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington.

JC857 U.S. PTO

60/471797



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**FEE TRANSMITTAL
for FY 2003**

Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27**TOTAL AMOUNT OF PAYMENT (\$)** 160.00**Complete if Known**

Application Number	UNKNOWN
Filing Date	CONCURRENTLY HEREWITH
First Named Inventor	CHARLES D. LANG
Examiner Name	UNKNOWN
Group / Art Unit	UNKNOWN
Attorney Docket No.	UC0330 US PRV

METHOD OF PAYMENT (check all that apply)
☐ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None
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04-1928

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E. I. du Pont de Nemours and Company

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FEE CALCULATION**1. BASIC FILING FEE**

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
1001	750	2001	375	Utility filing fee	
1002	330	2002	165	Design filing fee	
1003	520	2003	260	Plant filing fee	
1004	750	2004	375	Reissue filing fee	
1005	160	2005	80	Provisional filing fee	160
SUBTOTAL (1)					(\$) 160.00

2. EXTRA CLAIM FEES

2. SERVICE CHARGE		Extra Claims	Fee from below	Fee Paid
Total Claims	<input type="text"/> -20 **	= <input type="text"/> 0	X <input type="text"/> 18	= <input type="text"/> 0
Independent Claims	<input type="text"/> -3 **	= <input type="text"/> 0	X <input type="text"/> 84	= <input type="text"/> 0
Multiple Dependent	<input type="text"/>		X <input type="text"/> 280	= <input type="text"/>

Large Entity		Small Entity		Fee Description
Fee Code	Fee (\$)	Fee Code	Fee (\$)	
1202	18	2202	9	Claims in excess of 20
1201	84	2201	42	Independent claims in excess of 3
1203	280	2203	140	Multiple dependent claim, if not paid
1204	84	2204	42	** Reissue independent claims over original patent
1205	18	2205	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) (\$)

0.00

**or number previously paid, if greater; For Reissues, see above

FEE CALCULATION (continued)**3. ADDITIONAL FEES**

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
1051	130	2051	65	Surcharge - late filing fee or oath	
1052	50	2052	25	Surcharge - late provisional filing fee or cover sheet	
1053	130	2053	130	Non-English specification	
1812	2,520	1812	2,520	For filing a request for reexamination	
1804	920*	1804	920*	Requesting publication of SIR prior to Examiner action	
1805	1,840*	1805	1,840*	Requesting publication of SIR after Examiner action	
1251	110	2251	55	Extension for reply within first month	
1252	410	2252	205	Extension for reply within second month	
1253	930	2253	465	Extension for reply within third month	
1254	1,450	2254	725	Extension for reply within fourth month	
1255	1,970	2255	985	Extension for reply within fifth month	
1401	320	2401	160	Notice of Appeal	
1402	320	2402	160	Filing a brief in support of an appeal	
1403	280	2403	140	Request for oral hearing	
1451	1,510	1451	1,510	Petition to Institute a public use proceeding	
1452	110	2452	55	Petition to revive - unavoidable	
1453	1,300	2453	650	Petition to revive - unintentional	
1501	1,300	2501	650	Utility issue fee (or reissue)	
1502	470	2502	235	Design issue fee	
1503	630	2503	315	Plant issue fee	
1460	130	1460	130	Petitions to the Commissioner	
1807	50	1807	50	Processing fee under 37 CFR 1.17 (q)	
1808	180	1808	180	Submission of Information Disclosure Stmt	
8021	40	8021	40	Recording each patent assignment per property (times number of properties)	
1809	750	2809	375	Filing a submission after final rejection (37 CFR § 1.129(a))	
1810	740	2810	370	For each additional invention to be examined (37 CFR § 1.129(b))	
1801	760	2801	375	Request for Continued Examination (RCE)	
1802	900	1802	900	Request for expedited examination of a design application	

Other fee (specify)

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$)

0.00

SUBMITTED BY**Complete (if applicable)**

Name (Print/Type)	Thomas H. Magee, Reg. No. 27,355 for MARY ANN CAPRIA	Registration No. (Attorney/Agent)	32,659	Telephone	302-992-3749
Signature	<i>Thomas H. Magee</i>		Date	MAY 19, 2003	

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TITLEHOLE INJECTION LAYER WITH IMPROVED PERFORMANCE FOR
POLYMER LIGHT EMITTING DIODE DISPLAYS

5 A defect forms between anode lines of a passive matrix-addressed polymer light emitting displays (PLEDs) when adjacent lines are held in "on" and "off" states. The current invention addresses this defect.

 A PLED typically includes the following layers:

- a glass or plastic substrate;
- 10 a transparent conductive anode, e.g., indium tin oxide (ITO);
- a transparent electrically conductive polymer layer for injecting holes;
- an emissive polymeric layer;
- a cathode for injecting electrons;
- 15 a cover to exclude oxygen and moisture.

 PLED's may be designed to fulfill various types of lighting or display applications: lights and backlights, pixilated displays (passive & active matrix), segmented displays, icons, etc. The transparent conductive polymer layer (3) serves a number of purposes, including: injecting holes
20 into the emissive material, reducing the voltage drop due to differences in the anode and emissive layer work functions, planarizing steps etched in the anode layer, and covering surface defects on the anode. This polymer layer (3) is commonly termed a hole injection layer or, more generally, a buffer layer.

25 Many display applications take advantage of the relatively low electrical conductivity of the buffer layer by covering all the anode electrodes with a single layer of buffer polymer. Low electrical conductivity prevents shorting and "cross talk" between anodes that are held at different voltages. For example, in a passive matrix display adjacent
30 anode lines may be held at voltages corresponding to states of "off" and "on." The electrical conductivity of the buffer layer must be low enough that negligible current flows between these anode lines. However, if ions in the buffer layer polymer migrate due to the difference in electrical potential the buffer material will behave as an electrolyte between the anodes.
35 Depending on the physical structure of the buffer material (e.g., free volume, viscosity), and on the types and concentrations of the ionically conducting species, the region between the "on" and "off" anodes becomes deactivated, starting from the side nearest the "off" anode. When

the anodes are arranged as the columns of a pixilated display this defect manifests as apparent growth of the dark region between emissive columns. We term this defect "wide column gap" (WCG).

5 The WCG defect described here can be created anywhere on the display where two adjacent anode lines are biased at "on" and "off" voltages. Additionally, the WCG defect is, to some extent, reversible and the degraded area recovers when the anodes are returned to a common voltage. We attribute this defect to migration of ions due to the voltage difference between anodes in the "off" and "on" states. Recovery of the
10 area degraded by the WCG defect can sometimes be accelerated by inverting the image so the "on" and "off" voltages now drive ionically conducting species in the opposite directions.

It is the purpose of this invention to minimize or eliminate the WCG defect in a way that does not compromise other aspects of PLED
15 performance. Minimizing the defect includes preventing and/or delaying its formation, and maximizing recovery of the affected area.

Unexpectedly we find that addition of metal ions to the buffer layer also has a beneficial impact on WCG. We find the growth rate and extent of the WCG defect depends on the difference between the "on" and "off"
20 voltages (driving voltage for forming the defect), the physical structure of the buffer layer, and the types and concentrations of the ionically conducting species. The completeness of recovery from the WCG depends mainly on the type and concentration of the ionically conducting species.

25 We have found the tendency to form a WCG defect can be modified by changing the physical structure of the buffer layer, and by introducing suitable ionically conductive species. By physical structure we mean the state of the polymer chains – the relationship in space of various subunits or side chains, the degree of entanglement, the amount of free volume
30 trapped in the structure, etc.

There are numerous means for adjusting the physical structure of a polymer layer, e.g., annealing with heat above the T_g. When polymer layers are deposited from suspensions significant free volume can be frozen into the coalesced film depending on drying conditions and the
35 polymer T_g. It is widely practiced in paint and coating formulation to add co-solvents to the suspension so a polymer structure with reduced free volume is obtained after drying. Use of appropriate co-solvents to improve compatibility of polymers in a solution or suspension can lead to

improvements in polymer physical properties not possible by thermal annealing after deposition.

EXAMPLES

5 In the following examples a passive matrix PLED display was fabricated with the following components:

- 1) a substrate of 0.7 mm thick soda lime glass possessing a SiO₂ ion barrier layer;
- 10 2) an ITO conductive layer, nominally 1200Å thick, that was patterned into anode lines (columns) with a conductor nominally 370 microns wide, and with a nominal 50 micron gap between the conductive columns;
- 15 3) a transparent electrically conductive buffer layer of PEDOT, (Baytron P® VP CH8000 from H.C. Starck), nominally 2000Å thick after coating and drying, which was doped with various ionically conductive materials to modify the formation of the wide column gap defect;
- 4) an emissive polymeric layer, Covion SY, nominally 700Å thick after coating and drying;
- 20 5) a cathode for injecting electrons consisting of nominally 30Å of barium and 3500Å of aluminum;
- 25 6) a soda lime glass cover to exclude oxygen and moisture. The cover is glued to the display via a uv curable epoxy. A desiccant was placed between the lid and the aluminum layer of the cathode to prevent degradation of the display due to water permeation through the epoxy seal during the tests.

30 In addition to doping the PEDOT layer with ionically conductive species, we also varied the carrier fluid used for coating the PEDOT by adding a mixture of cosolvents designed to modify the drying and resulting polymeric matrix. In the examples below the term cosolvent is meant to indicate addition of a mixture containing normal propyl alcohol (nPA) and 1-methoxy-2-propanol (1M2P) so the levels in the cosolvents in the coating solution were 10% nPA and 15% 1M2P by volume. The PEDOT solution was nominally 2.8% solids by weight before addition of the
35 cosolvent blend.

Displays cells described above were fabricated as described above, and tested as described below. The suspension of PEDOT used in these experiments was Baytron P® VP CH8000, lot CHDSPP002. It was ca.

2.87% solids by weight and contained ca. 270 ppm Na⁺ ions as supplied by the vendor, corresponding to ca. 0.4 mmol Na⁺ per gram of dried polymer (mmol/g). The concentration of metal ions was adjusted as described below.

5 The WCG defect was induced by either imposing a DC voltage difference across adjacent anode lines (vertical columns in the pictures). The anode voltages in the "on" and "off" states were as shown below. The extent of the WCG defect was assessed after the times shown.

10 The examples below show how adjusting the buffer solution with cosolvents (a temporary change) and donor salts (a permanent) change affect the formation and recovery of the WCG defect. Where donor concentrations exceed the ~0.4 mmol/g of sodium native in the PEDOT as received the levels were adjusted using the salts shown in parentheses in the table. For examples 1-4 adjacent anode lines (columns) were held at
15 the voltage difference show in the tables, and the severity of the WCG defect was evaluated visually.

Example 1

20 Displays were made as described above with PEDOT solution as received from the vendor, and a dionized version of PEDOT solution. It was noted that the WCG defect formed very rapidly with these PEDOT samples and was not affected by the voltage or time combinations shown. Deionizing the PEDOT solution clearly leads to inferior performance.

<u>Buffer solution Composition</u>	<u>Approximate dopant concentration, mmol/g dried polymer</u>	<u>Test conditions</u>	<u>Severity (0=none, 5=worst)</u>
PEDOT as received	0.4 Na ⁺	14 V for 30 minutes	4
PEDOT as received	0.4 Na ⁺	14 V for 60 minutes	4
PEDOT as received	0.4 Na ⁺	20 V for 20 minutes	4
PEDOT as received	0.4 Na ⁺	20 V for 120 minutes	4
Dionized PEDOT	<0.001 Na ⁺	14 V for 60 minutes	5

25

Example 2

Displays were made as described above with various concentrations of metal ions, provided by the salts shown in the table. The performance of different metal ions is essentially equivalent.

30

<u>Buffer solution Composition</u>	<u>Approximate dopant concentration, mmol/g dried polymer</u>	<u>Test conditions</u>	<u>Severity (0=none, 5=worst)</u>
PEDOT as received	0.4 Na ⁺	14 V for 30 minutes	4
Doped PEDOT	0.4 Na ⁺ + 0.6 K ⁺ (from KCl)	14 V for 30 minutes	2
Doped PEDOT	0.4 Na ⁺ + 0.6 Mg ²⁺ (from MgSO ₄)	14 V for 30 minutes	2
Doped PEDOT	0.4 Na ⁺ + 0.6 Cs ⁺ (from Cs ₂ CO ₃)	14 V for 30 minutes	2
Doped PEDOT	0.7 Na ⁺ (0.3 from NaCl)	14 V for 30 minutes	2

Example 3

Displays were made as described above with various concentrations of metal ions, provided by the salts shown in the table. Cosolvents were added to the PEDOT solution modify the physical properties of the PEDOT layer; the cosolvents were removed completely by drying in air on a hot plate at 200C for 3 minutes, then under vacuum at 80C for 5 minutes. The test conditions were made more severe by increasing the voltage difference and the length of the test to exacerbate the defect; hence the ratings in this table (except for "PEDOT as received") cannot be compared directly with previous examples. Addition of cosolvent reduces the defect severity. When cosolvent is present one can reduce or eliminate the WCG defect with relatively low levels of dopant. (It appears NaCl is a superior donor salt vs. NaOH or Na₂CO₃, but as shown below we find NaCl is not preferred.) Levels of salt that eliminate the WCG (without cosolvent) are also shown for reference.

<u>Buffer solution Composition</u>	<u>Approximate dopant concentration, mmol/g dried polymer</u>	<u>Test conditions</u>	<u>Severity (0=none, 5=worst)</u>
PEDOT as received	0.4 Na ⁺	20 V for 20 minutes	4
PEDOT + cosolvents	0.4 Na ⁺	20 V for 60 minutes	3
Doped PEDOT + cosolvents	0.8 Na ⁺ (0.4 from NaOH)	20 V for 60 minutes	1
Doped PEDOT + cosolvents	0.8 Na ⁺ (0.4 from Na ₂ CO ₃)	20 V for 60 minutes	1
Doped PEDOT + cosolvents	1.2 Na ⁺ (0.8 from NaOH)	20 V for 60 minutes	1
Doped PEDOT + cosolvents	0.8 Na ⁺ (0.4 from NaCl)	20 V for 60 minutes	0
Doped PEDOT	2.0 Na ⁺ (1.6 from NaOH)	20 V for 120 minutes	0
Doped PEDOT	3.0 Na ⁺ (2.6 from NaOH)	20 V for 120 minutes	0

Example 4

Above approximately 3 mmol/g of sodium ions the electrical performance of the display begins to deteriorate. (Other limitations may exist depending on the donor salt. For example, when the donor is NaOH the amount that can be introduced into PEDOT solution is limited by the resulting increase in pH. Typically above pH~2 the solution becomes unstable and the resulting coated layer is not acceptable for a high quality display.) This example shows that when the test conditions are made severe enough the WCG defect cannot be eliminated with acceptable levels of salt, with or without cosolvent.

<u>Buffer solution Composition</u>	<u>Approximate dopant concentration, mmol/g dried polymer</u>	<u>Test conditions</u>	<u>Severity (0=none, 5=worst)</u>
Doped PEDOT	2.0 Na+ (1.6 from NaOH)	30 V for 5 hours	1
Doped PEDOT + cosolvents	2.0 Na+ (1.6 from NaOH)	30 V for 5 hours	1
Doped PEDOT	3.0 Na+ (2.6 from NaOH)	30 V for 14 hours	1
Doped PEDOT + cosolvents	3.0 Na+ (2.6 from NaOH)	30 V for 14 hours	1

Example 5

To better simulate the actual impact of dopants and cosolvent on a display the following compositions were made into displays and driven to simulate a multiplex mode of operation using a Solomon 1301 driver. In this mode of operation the adjacent anode columns were held at voltage difference of ca. 12.3 V, and the row (cathode) voltages were scanned at a rate of 80 Hz. The row "on" voltages were adjusted to achieve a brightness level of ca. 200 cd/m². (This did not affect the voltage difference across the anode column lines.) The displays were tested in this mode for 82 hours and the severity of the defect was noted as shown below. The displays were tested in this manner for a total of 101 hours of operation with no further increase in the severity of the WCG defect. After 101 hours of operation the displays were turned off and allowed to recover for ca. 16 hours; they were then lit briefly to inspect for the extent of recovery. This example shows the inferior performance of NaCl as a donor for the dopant ions. The ratings in this test are unrelated to any of the previous examples.

<u>Buffer composition</u>	<u>Approximate dopant concentration, mmol/g dried polymer</u>	<u>Severity, 0=none, 5=worst</u>	<u>Severity after 16 hr recovery</u>
PEDOT as received	0.4 Na+	5	5
PEDOT + cosolvents	0.4 Na+	4	4
Doped PEDOT + cosolvents	0.8 Na+ (0.4 from NaOH)	3	1
Doped PEDOT + cosolvents	0.8 Na+ (0.4 from Na ₂ CO ₃)	3	1
Doped PEDOT + cosolvents	0.8 Na+ (0.4 from NaCl)	3	3
Doped PEDOT + cosolvents	1.2 Na+ (0.8 from Na ₂ CO ₃)	2	1